found at 233° and 302°, but both sets of values show the degree of dispersion of the metal in the film to be very great. The particles are small enough therefore to assume forms in which the influence of surface tension predominates.

I hope to improve the method of investigation by employing films of the attackable metals deposited on an inert metal.

On Measurements of Electrode Potential Drop with Direct Current and Alternating Current Electrolysis.

By S. Marsh, B.Sc., Ph.D., and A. E. Evans, B.Sc.

(Communicated by E. H. Griffiths, F.R.S. Received April 29, 1922.)

§1.

The investigations to be described in this paper are the outcome of some work by one of the authors on alternating current electrolysis,* in which the behaviour of platinum, gold and nickel electrodes, using dilute sulphuric acid and barium hydrate solution as electrolytes, was examined for alternating current with frequencies lying between 25 cycles and 80 cycles per second. Some provisional measurements of the electrode drop were made at that time, but it was felt desirable to examine this feature in greater detail.

The apparatus employed for the purpose is shown in fig. 1. The electrolyte was contained in a glass tube EF, 60 cm. long and 4 cm. diameter, provided with a feed tube D. The ends were closed with rubber stoppers, each pierced with two holes, through which passed tubes holding electrodes A and C and an "explorer" B, and a thermometer T. The electrode C was of platinum, and remained unchanged throughout all the experiments.

A was the experimental electrode, rectangular in shape, area approximately 0·4 sq. cm. Electrodes of double and half this area were also employed to investigate the effect of current density.

It was attached to a short platinum wire which was sealed through the tube, and electrical contact was made by mercury with wires from the supply. The "explorer" B consisted of a fine platinum wire (0·05 mm. diameter) which projected about 1 or 2 mm. from a fine glass tube sealed at B. The distance AB was approximately 1 mm. in all cases. Contact was made with mercury as before.

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* S. Marsh, 'Roy. Soc. Proc.,' A, vol. 97, pp. 124–144.

Alternating current was supplied from a small Westinghouse motor-generator set up to 40 cycles per second, and from a Crompton machine for frequencies up to 80 cycles per second.

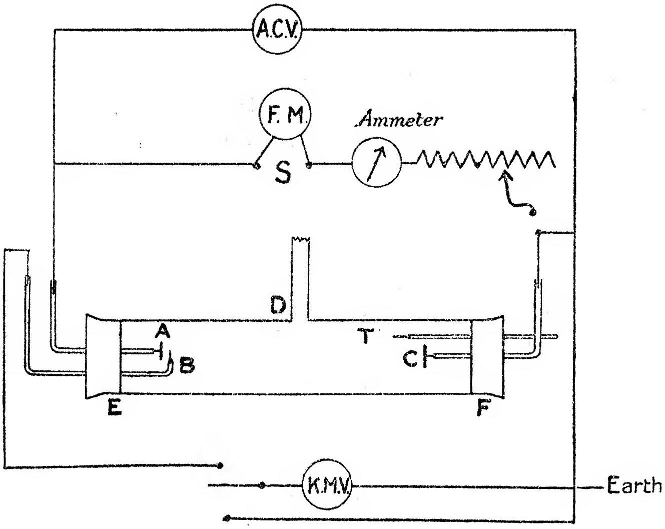

Fig. 1.

The arrangements for the measurement of electrode drop are also shown in fig. 1. The difference in potential between A and B is too small (at any rate when alternating current is used) to allow of direct measurement. It was necessary, therefore, to make simultaneous readings of the potential difference between A and C, and B and C. That between A and C was determined by a Weston standard alternating (and direct) current voltmeter reading to 0·01 volt.

The potential drop between B and C was obtained by a Kelvin multicellular electrostatic voltmeter. As the scale of the latter commenced at 40 volts, while the potential drop from B to C was of the order of 10 volts, a small mirror was fixed to a new and more sensitive suspension, and readings made by lamp and scale. The Kelvin instrument was calibrated both with direct and alternating current, and the results were in excellent agreement.

Experiment showed that a current of 0·4 ampère gave readings on the open part of the scale of the multicellular instrument, and, as a consequence, this value of the current was employed throughout. The current density in most cases was approximately 0·5 ampère per square centimetre, counting both faces of the electrode.

The multicellular voltmeter was much more sluggish in its movements than the Weston voltmeter, and in order to reduce any error arising from this cause, the current through the tube was carefully maintained at 0·4 ampère throughout the experiment. The frequency was kept at a constant value as registered on a Hartmann-Braun frequency-meter. Readings were taken every minute on the voltmeters.

A direct determination of the potential drop from A to B is desirable, but its magnitude (usually less than 1 volt) is too small for detection by ordinary methods when alternating current is employed.

Calculation has shown that it would be possible to measure potential differences of that order by means of an electrostatic oscillograph in which low velocity cathode rays produced from a Wehnelt cathode are deflected in passing between condenser plates connected to A and B, and it is hoped to proceed further with the construction of such an instrument.

Normal sulphuric acid was employed throughout as the electrolyte, fresh acid being used for each experiment, while the electrodes consisted of polished platinum, platinum black, gold and nickel.

§ 2.

Summary of Results with Direct Current.

Electrode Acting as Cathode.

The relation of electrode drop to time is indicated in fig. 2, where typical curves are represented for the various metals. Too much importance must not be paid to the actual magnitudes involved, since repetition of an experiment under identical circumstances did not lead, as a rule, to the same quantitative results. The *type* of curve was, however, the same in repetition experiments.

It will be noticed that with platinum, gold and nickel electrodes, the cathode drop increases with time, the curves, especially those for polished platinum, being similar in type to the saturation curves in radio-activity. With platinum, the electrode drop becomes approximately constant after 30 minutes. In the case of gold, the increase is not so much as with platinum, and in one case there is a suggestion of a second rise after about 60 minutes.

With platinum black electrodes, the increase in the electrode drop is more gradual. The evidence, in the case of nickel electrodes, is somewhat conflicting, but the curves on the whole resemble those for platinum and gold.

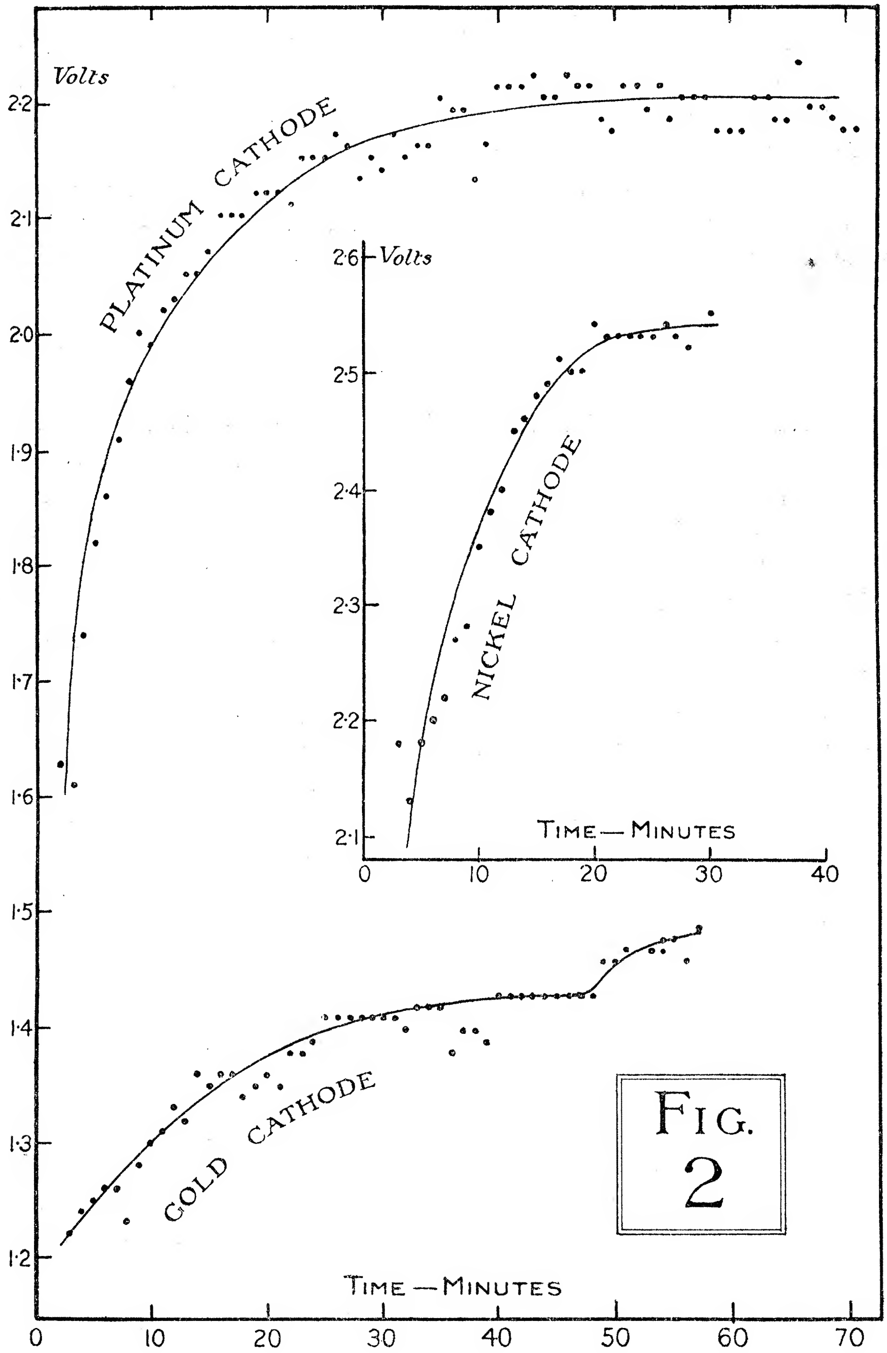
Volts
2·2
2·1
2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
PLATINUM CATHODE
GOLD CATHODE
TIME — MINUTES
0
10
20
30
40
50
60
70
2·6
Volts
2·5
2·4
2·3
2·2
2·1
NICKEL CATHODE
TIME — MINUTES
0
10
20
30
40

FIG. 2

Electrode Acting as Anode.

Typical curves are shown in fig. 3. With polished platinum, the electrode drop decreases until about the 40th minute and then rises. The rates of fall and rise are approximately the same, as are also the amounts of ascent and descent.

In the case of gold, the rate of descent is slightly more rapid and the amount of ascent smaller than the total fall. With platinum black, the variations of electrode drop are not so marked.

§ 3.

Results with Alternating Currents.

As will be seen from fig. 4, the variation of electrode drop with time is very irregular, and there is considerable divergence from the smooth curve drawn to lie evenly between the points. It is, of course, obvious that in this case the ordinates do not measure electrode fall in the same sense as with direct current, for the electrode is alternately anode and cathode; and furthermore, the ordinates represent the differences between simultaneous readings on the alternating current voltmeter across AC and the Kelvin instrument across BC.

Hence the importance of setting up, if possible, a low voltage electrostatic oscillograph, and reading directly the drop between A and B. This voltage would furnish, in addition, a knowledge of the *form* of the wave curve.

Platinum.—For the frequencies examined (25 to 80) the electrode drop decreases during an interval—the length of which depends upon the frequency of the alternating current—and thereafter increases slightly. This is summarised in the following table:—

Size of electrode.	Frequency.	Time to reach minimum electrode drop.
Full	25 cycles.	40 mins.
,,	33·5 ,,	30 ,,
,,	45 ,,	25 ,,
,,	60 ,,	30 ,,
,,	80 ,,	15 ,,
Half	25 ,,	100 ,,
,,	33·5 ,,	60 ,,
Double	25 ,,	40 ,,
,,	33·5 ,,	27·5 ,,

Gold.—There is the same general tendency as with platinum except that the minimum is reached somewhat earlier.

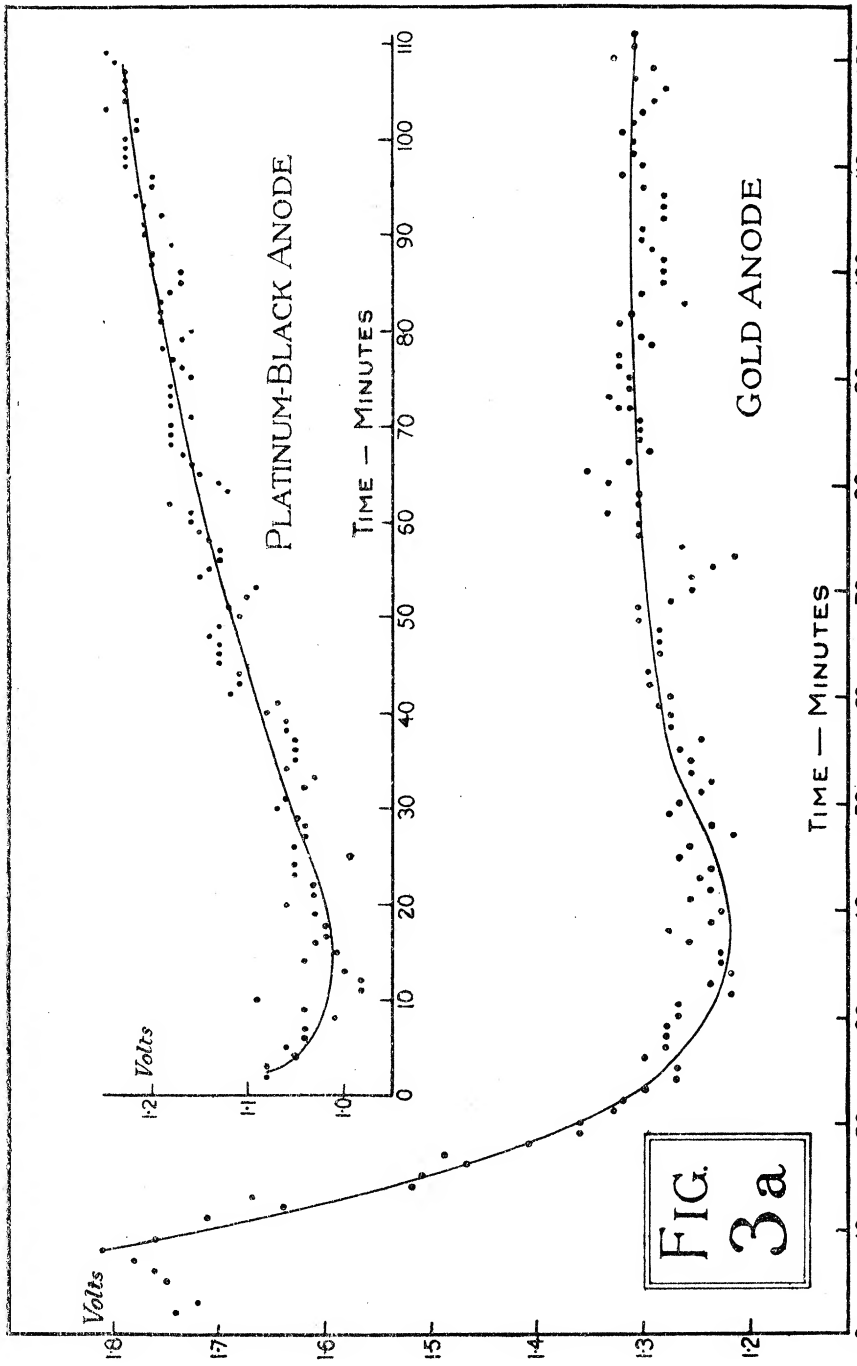
Volts
1·8
1·7
1·6
1·5
1·4
1·3
1·2
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME — MINUTES
GOLD ANODE
PLATINUM-BLACK ANODE
Volts
1·2
1·1
1·0
0
10
20
30
40
50
60
70
80
90
100
110
TIME — MINUTES

FIG. 3a

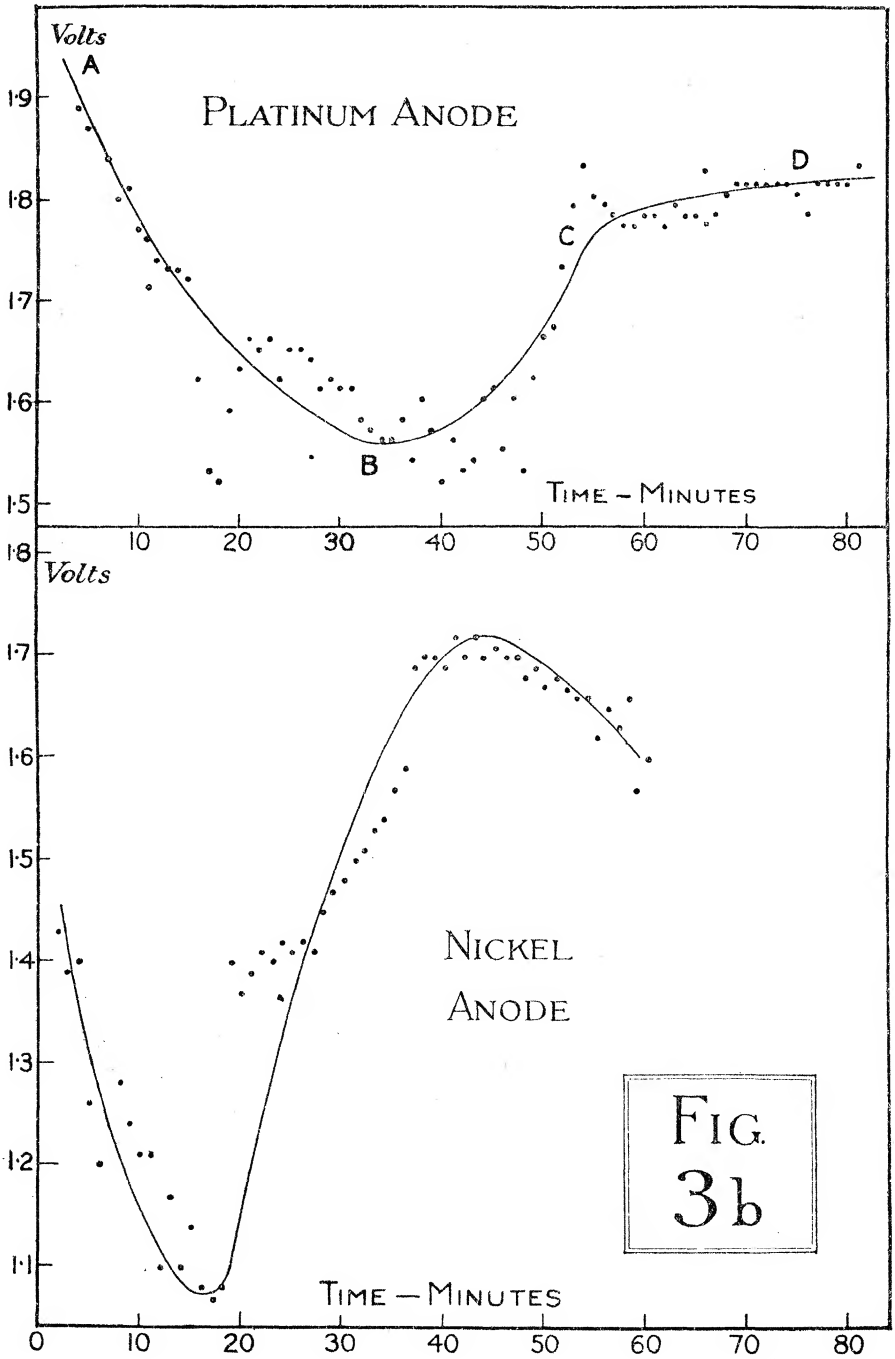
Volts
A
PLATINUM ANODE
D
C
B
1·9
1·8
1·7
1·6
1·5
TIME – MINUTES
10
20
30
40
50
60
70
80
1·8
Volts
1·7
1·6
1·5
1·4
1·3
1·2
1·1
NICKEL
ANODE
TIME — MINUTES
0
10
20
30
40
50
60
70
80

FIG. 3b

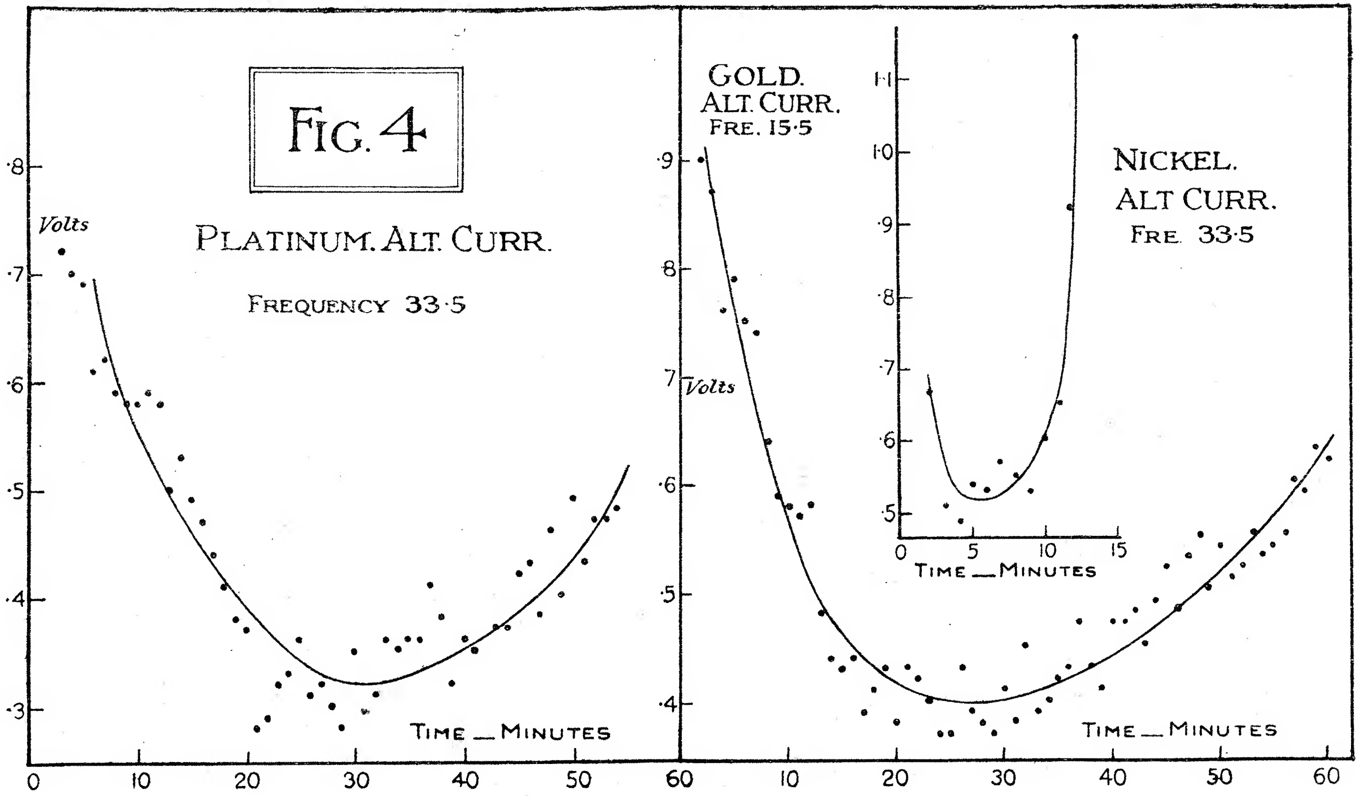
FIG. 4

PLATINUM. ALT. CURR.
FREQUENCY 33·5

GOLD.
ALT. CURR.
FRE. 15·5

NICKEL.
ALT CURR.
FRE. 33·5

Nickel.—The decrease and subsequent rise is much more rapid than with gold and platinum. The very sudden ascent is due to the solution of the electrode in the electrolyte and the consequent increase in current density.

Black Platinum.—In the majority of cases the readings, though very irregular, suggest a more or less steady voltage.

§ 4.

Discussion of Results.

The phenomena occurring with direct current electrolysis will first be examined. As the measurements are made during the actual passage of the current, the results are not to be confused with the measurements of the ordinary contact difference of potential between metal and acid.

The phenomena taking place at an electrode comprise :—

(1) The evolution of gas, which coats the surface of the electrode with a film of bubbles ;

(2) Absorption and adsorption of gas by the electrode ;

(3) Oxidation of the electrode (in the case of an anode) or formation of hydrides (with cathode) ;

(4) Chemical changes in the electrolyte.

The effect due to (1) above will be, at any rate with direct current, of a fairly constant nature.

Electrode Acting as Cathode.

The gas entering the electrode, being in the ionic state, has a tendency to re-enter the electrolyte, and so sets up a back e.m.f., whose magnitude depends upon the quantity of gas occluded. This quantity will increase with time, the relation between amount occluded and time being represented approximately by a curve of the "saturation" type. It is reasonable to assume that the back e.m.f. will vary in a similar manner, and hence the curves representing the relation of electrode drop to time will be of the type shown in fig. 2.

The more quickly the surface layers of the electrode become saturated with the gas the more rapid will be the consequent increase in electrode drop. With a prepared surface of great area, such as platinum black, it would be possible for occlusion to go on for a considerable period before the metal gets saturated. Hence, we should anticipate a lower initial electrode drop and a smaller rate of increase with time.

It is obvious that any agency which tends to break up the surface, thus exposing a greater area to the action of the gas, will facilitate occlusion, and it is highly probable that the disintegration of the surface, which takes place with alternating current electrolysis, has a very important bearing on the electrode drop in such cases.

Since more gas is occluded by platinum than gold, we should expect that the rise in the electrode drop would be greater in the case of platinum than with gold. This is confirmed by experiment.

Electrode Acting as Anode.

In this case oxidation and occlusion are going on simultaneously, but for the sake of simplicity, we consider these processes separately. We conceive, then, that oxidation of the surface layer of the metal takes place, and that in consequence of the disintegration of surface thereby produced a larger area of metal surface is exposed to the action of the gas, thus allowing oxidation to proceed at an increasing rate.

The surface XY of pure metal (fig. 5), exposed to the action of the gas, would gradually increase up to a maximum; as a consequence, the rate of removal of ionised gas at the metal face, by combination, would also increase to a maximum, and the electrode drop, on this account, would fall to a minimum value.

As the thickness of the oxidised layer increases, however, the amount of ionised gas reaching the virgin surface XY per second becomes smaller, owing to absorption in the layer of oxide to the left of XY. This gradual accumulation of gas in the oxide will produce an increasing back e.m.f. similar in type to that occurring when the electrode acts as cathode.

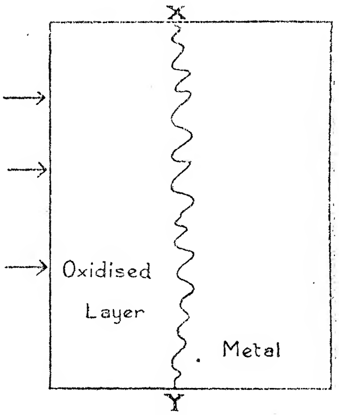

FIG. 5.

Thus in fig. 3, the portion AB of the potential-time curve is attributed to the effect of oxidation, while BCD represents the state of things when the removal of gas by oxidation is more than nullified by the gradual accumulation of gas in the surface layers.

If the film of oxide became detached mechanically or dissolved in the electrolyte, then it is conceivable that oxidation at the metal face would gain the upper hand for a time, and the curve repeat itself. There have been indications of such curves with platinum.

With a platinum black electrode, oxidation would proceed immediately at the maximum rate at the prepared surface; in other words, the initial electrode drop would be smaller than with polished platinum. Occlusion would come into action earlier so that we should expect that the portion AB of the curve in fig. 3 would be much less pronounced, and that the increase in the electrode drop would occur earlier. The experimental results lend support to these suggestions.

In the case of gold, the portion AB of the curve is very pronounced, but the portion BC is not nearly so marked as with platinum. This would indicate that occlusion plays a much less prominent part with gold than with platinum.

In the case of nickel, it must be remembered that the oxide formed is soluble in the acid,* and the metallic surface is roughened, exposing consequently a larger area for oxidation. Hence, the initial drop AB in the curve would be expected. The gradual accumulation of gas in the surface layers of the nickel (or of the oxide, if the metal is oxidised at a greater rate than it can be dissolved) would give rise to the portion BC of the curve.

§ 5.

Phenomena with Alternating Current.

There is evidence that the minimum electrode drop is reached sooner with high than with low frequencies (see Table, p. 332).

In addition to the processes of oxidation and occlusion already discussed with direct current electrolysis, there is the chemical action between the gases liberated in each half-cycle and those present, either in a state of occlusion in, or in combination with, the electrode.

During the first anodic half-period some oxidation occurs, and, in addition, some oxygen enters the electrode. In the succeeding half-period, the hydrogen liberated reduces the oxide and combines with the oxygen occluded in the oxide; in addition, some hydrogen is retained at the surface, while some diffuses into the deeper layers. The oxygen of the third half-period is able, since the electrode surface is more broken up, to enter more readily. It combines with the hydrogen in the surface layers; oxidises these layers of spongy metal; and, in addition, diffuses into the layers beneath.

Since hydrogen diffuses more quickly than oxygen, the deeper layers gradually accumulate this gas. Hence, there is less tendency for the hydrogen liberated in later cathodic half-cycles to diffuse into these layers, and this hydrogen is confined to the layers nearer the surface, thus facilitating the removal of oxygen of anodic half-cycles.

Thus, as electrolysis proceeds, more and more of the gas produced in any half-period is used up, and finally (subject to conditions stated in the previous paper) evolution of gas ceases.

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* *Loc. cit.*, pp. 133, 138, § 7.

So far the action of the electrolyte has been neglected. During the anodic half-cycle, persulphuric acid is formed. Hence there is less oxygen available for oxidation and occlusion. Consequently, a surplus of hydrogen is left over after each cycle, so that even after gas evolution has ceased a gradual accumulation of hydrogen still goes on.

We should expect the electrode drop to follow the same sequence of changes as with the anodic fall with direct current, viz., it should decrease as more and more of the gas is removed by chemical action, and ultimately a slight rise should set in owing to the gradual accumulation of hydrogen in the electrode.

These effects have been observed in the great majority of cases with alternating current. Furthermore, it is interesting to record that the electrode drop reaches its minimum value at about the same time that the gases cease to be evolved. As the frequency increases, the more frequent oxidation and reduction will break up the surface layers more effectively, thus facilitating the recombination of the gases ; hence, the minimum electrode drop will be reached earlier.

Variation of Current Density.

With electrodes of increasing area (in other words, with decreasing current density), one would expect the surface effect (adsorption) to be more, and the diffusion effect to be less pronounced. Hence there is from the start a more effective recombination (or action) between the gases liberated in successive half-cycles, and we should expect the minimum electrode drop to be reached more quickly. (The subsequent rise also should be smaller, since, with a more pronounced surface effect, there will be less accumulation of hydrogen in the interior. There is ample confirmation of the first conclusion (see Table, p. 332), but the evidence for the second is not sufficiently definite.)

Effect of Different Metals.

The theory outlined above represents the general behaviour of all the metals examined. Taking polished platinum as typical, the following minor differences will be noticed between it and the other metals :—

Gold.—The results with direct current indicate that the effect of oxidation is more pronounced than that of occlusion. The surface effect referred to above should have greater influence than diffusion, and the minimum electrode fall should be reached more quickly than with platinum, and the subsequent rise should be smaller.

Nickel.—Solution occurs, the rate of solution increasing with frequency. Solution of the electrode is equivalent to a rapid increase in the current density, and we should expect the diffusion effect to be pronounced. The electrode would get saturated with hydrogen and would offer a big back e.m.f.

Experiment shows that the initial drop is followed by a very sudden rise as the electrode dissolves.

Platinum-Black.—Owing to the prepared surface, the rate of recombination should be very great from the commencement. No gases, in fact, are evolved with alternating current.

Experiment shows that the electrode fall is more or less steady.

Summary.

The variation with time of the electrode potential drop of various metals has been examined both with direct and alternating current. An attempt has been made to interpret these variations as being due to oxidation and occlusion phenomena within the electrodes. The conclusions confirm the results of the previous investigation on the volume of gases evolved during alternating current electrolysis.

We desire to express our thanks to Dr. E. H. Griffiths, F.R.S., for his interest in the paper, and to Mr. W. H. Sewell for his assistance in taking the observations.

Variation of the Intensity of Reflected X-Radiation with the Temperature of the Crystal.

By Ivor Backhurst, B.Sc.

(Communicated by Sir William Bragg, K.B.E., F.R.S. Received August 29, 1922.)

On account of the increasing importance of the temperature factor in the theory of the analysis of crystal structure by means of X-ray reflection, and in view of the fact that no experimental work on the temperature effect has been published since the original preliminary investigation by Prof. W. H. Bragg* in 1914, it is hoped that the present account will be of interest, in which the work of Bragg is extended to a variety of crystals and continuous temperature curves have been obtained ranging up to 950° C.

* See "X-Rays and Crystal Structure," by Sir William Bragg and W. L. Bragg, also 'Phil. Mag.,' May, 1914.